

09/622299

Practitioner's Docket No. HES 2 0001

CHAPTER II

**TRANSMITTAL LETTER
TO THE UNITED STATES ELECTED OFFICE (EO/US)**

(ENTRY INTO U.S. NATIONAL PHASE UNDER CHAPTER II)

PCT/IL99/00097	16 February 1999	26 February 1998
INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES		
TITLE OF INVENTION		
GARTI, Nissim and BERKOVICH, Yana		
APPLICANT(S)		

Box PCT
Assistant Commissioner for Patents
Washington D.C. 20231

ATTENTION: EO/US

NOTE: To avoid abandonment of the application, the applicant shall furnish to the USPTO, not later than 20 months from the priority date: (1) a copy of the international application, unless it has been previously communicated by the International Bureau or unless it was originally filed in the USPTO; and (2) the basic national fee (see 37 C.F.R. § 1.492(a)). The 30-month time limit may not be extended. 37 C.F.R. § 1.495.

CERTIFICATION UNDER 37 C.F.R. § 1.10*
(Express Mail label number is mandatory.)
(Express Mail certification is optional.)

I hereby certify that this Transmittal Letter and the papers indicated as being transmitted therewith is being deposited with the United States Postal Service on this date August 15 2000, in an envelope as "Express Mail Post Office to Addressee" Mailing Label Number EL530411122US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

BENJAMIN TRELLA

(type or print name of person mailing paper)


Signature of person mailing paper

WARNING: Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. § 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

***WARNING:** Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. § 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

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WARNING: Where the items are those which can be submitted to complete the entry of the international application into the national phase are subsequent to 30 months from the priority date the application is still considered to be in the international state and if mailing procedures are utilized to obtain a date the express mail procedure of 37 C.F.R. § 1.10 must be used (since international application papers are not covered by an ordinary certificate of mailing - See 37 C.F.R. § 1.8.

NOTE: Documents and fees must be clearly identified as a submission to enter the national state under 35 U.S.C. § 371 otherwise the submission will be considered as being made under 35 U.S.C. § 111. 37 C.F.R. § 1.494(f).

- I. Applicant herewith submits to the United States Elected Office (EO/US) the following items under 35 U.S.C. § 371:
- ☒ This express request to immediately begin national examination procedures (35 U.S.C. § 371(f)).
 - ☒ The U.S. National Fee (35 U.S.C. § 371(c)(1)) and other fees (37 C.F.R. § 1.492) as indicated below:

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2. Fees

CLAIMS FEE	(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
<input type="checkbox"/> *	TOTAL CLAIMS	19 -20=	-0-	× \$18.00=	\$ -0-
	INDEPENDENT CLAIMS	1 -3=	-0-	× \$78.00=	-0-
	MULTIPLE DEPENDENT CLAIM(S) (if applicable) + \$260.00				
BASIC FEE**	<input type="checkbox"/> U.S. PTO WAS INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where an international preliminary examination fee as set forth in § 1.482 has been paid on the international application to the U.S. PTO: <input type="checkbox"/> and the international preliminary examination report states that the criteria of novelty, inventive step (non-obviousness) and industrial activity, as defined in PCT Article 33(1) to (4) have been satisfied for all the claims presented in the application entering the national stage (37 C.F.R. § 1.492(a)(4)) \$96.00 <input type="checkbox"/> and the above requirements are not met (37 C.F.R. § 1.492(a)(1)) \$670.00 <input checked="" type="checkbox"/> U.S. PTO WAS NOT INTERNATIONAL PRELIMINARY EXAMINATION AUTHORITY Where no international preliminary examination fee as set forth in § 1.482 has been paid to the U.S. PTO, and payment of an international search fee as set forth in § 1.445(a)(2) to the U.S. PTO: <input type="checkbox"/> has been paid (37 C.F.R. § 1.492(a)(2)) \$760.00 <input type="checkbox"/> has not been paid (37 C.F.R. § 1.492(a)(3)) \$970.00 <input type="checkbox"/> where a search report on the international application has been prepared by the European Patent Office or the Japanese Patent Office (37 C.F.R. § 1.492(a)(5)) \$840.00				\$840.00
	Total of above Calculations				=
SMALL ENTITY	Reduction by 1/2 for filing by small entity, if applicable. Affidavit must be filed also. (note 37 C.F.R. § 1.9, 1.27, 1.28)				-
	Subtotal				\$840.00
	Total National Fee				\$840.00
	Fee for recording the enclosed assignment document \$40.00 (37 C.F.R. § 1.21(h)). (See Item 13 below). See attached "ASSIGNMENT COVER SHEET".				
TOTAL	Total Fees enclosed				\$840.00

*See attached Preliminary Amendment Reducing the Number of Claims.

- i. ☒ A check in the amount of \$840.00 to cover the above fees is enclosed.
- ii. ☐ Please charge Account No. _____ in the amount of \$ _____.
A duplicate copy of this sheet is enclosed.

****WARNING:** "To avoid abandonment of the application the applicant shall furnish to the United States Patent and Trademark Office not later than the expiration of 30 months from the priority date: * * * (2) the basic national fee (see § 1.492(a)). The 30-month time limit may not be extended." 37 C.F.R. § 1.495(b).

WARNING: If the translation of the international application and/or the oath or declaration have not been submitted by the applicant within thirty (30) months from the priority date, such requirements may be met within a time period set by the Office. 37 C.F.R. § 1.495(b)(2). The payment of the surcharge set forth in § 1.492(e) is required as a condition for accepting the oath or declaration later than thirty (30) months after the priority date. The payment of the processing fee set forth in § 1.492(f) is required for acceptance of an English translation later than thirty (30) months after the priority date. Failure to comply with these requirements will result in abandonment of the application. The provisions of § 1.136 apply to the period which is set. Notice of Jan. 3, 1993, 1147 O.G. 29 to 40.

3. ☐ A copy of the International application as filed (35 U.S.C. § 371(c)(2)):

NOTE: Section 1.495 (b) was amended to require that the basic national fee and a copy of the international application must be filed with the Office by 30 months from the priority date to avoid abandonment. "The International Bureau normally provides the copy of the international application to the Office in accordance with PCT Article 20. At the same time, the International Bureau notifies applicant of the communication to the Office. In accordance with PCT Rule 47.1, that notice shall be accepted by all designated offices as conclusive evidence that the communication has duly taken place. Thus, if the applicant desires to enter the national stage, the applicant normally need only check to be sure the notice from the International Bureau has been received and then pay the basic national fee by 30 months from the priority date." Notice of Jan. 7, 1993, 1147 O.G. 29 to 40, at 35-36. See item 14c below.

- a. ☐ is transmitted herewith.
- b. ☐ is not required, as the application was filed with the United States Receiving Office.
- c. ☒ has been transmitted
- i. ☒ by the International Bureau. 23.03.99
Date of mailing of the application (from form PCT/1B/308): 23 March 1999
- ii. ☐ by applicant on _____.
Date

4. ☒ A translation of the International application into the English language (35 U.S.C. § 371(c)(2)):
- a. ☒ is transmitted herewith.
- b. ☐ is not required as the application was filed in English.
- c. ☐ was previously transmitted by applicant on _____.
Date
- d. ☐ will follow.

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5. ☒ Amendments to the claims of the International application under PCT Article 19 (35 U.S.C. § 371(c)(3)):

NOTE: The Notice of January 7, 1993 points out that 37 C.F.R. § 1.495(a) was amended to clarify the existing and continuing practice that PCT Article 19 amendments must be submitted by 30 months from the priority date and this deadline may not be extended. The Notice further advises that: "The failure to do so will not result in loss of the subject matter of the PCT Article 19 amendments. Applicant may submit that subject matter in a preliminary amendment filed under section 1.121. In many cases, filing an amendment under section 1.121 is preferable since grammatical or idiomatic errors may be corrected." 1147 O.G. 29-40, at 36.

- a. ☐ are transmitted herewith.
- b. ☒ have been transmitted
- i. ☒ by the International Bureau. 23.03.1999
Date of mailing of the amendment (from form PCT/1B/308): ~~23 March~~ 1999
- ii. ☐ by applicant on (date) _____.
Date
- c. ☐ have not been transmitted as
- i. ☐ applicant chose not to make amendments under PCT Article 19.
Date of mailing of Search Report (from form PCT/ISA/210.): _____
- ii. ☐ the time limit for the submission of amendments has not yet expired.
The amendments or a statement that amendments have not been made will be transmitted before the expiration of the time limit under PCT Rule 46.1.

6. ☒ A translation of the amendments to the claims under PCT Article 19 (38 U.S.C. § 371(c)(3)):
- a. ☒ is transmitted herewith.
- b. ☐ is not required as the amendments were made in the English language.
- c. ☐ has not been transmitted for reasons indicated at point 5(c) above.
7. ☒ A copy of the international examination report (PCT/IPEA/409)
- ☒ is transmitted herewith.
- ☐ is not required as the application was filed with the United States Receiving Office.
8. ☒ Annex(es) to the international preliminary examination report
- a. ☒ is/are transmitted herewith.
- b. ☐ is/are not required as the application was filed with the United States Receiving Office.
9. ☒ A translation of the annexes to the international preliminary examination report
- a. ☒ is transmitted herewith.
- b. ☐ is not required as the annexes are in the English language.

10. ☒ An oath or declaration of the inventor (35 U.S.C. § 371(c)(4)) complying with 35 U.S.C. § 115

a. ☐ was previously submitted by applicant on _____
Date

b. ☒ is submitted herewith, and such oath or declaration

i. ☒ is attached to the application.

ii. ☐ identifies the application and any amendments under PCT Article 19 that were transmitted as stated in points 3(b) or 3(c) and 5(b); and states that they were reviewed by the inventor as required by 37 C.F.R. § 1.70.

iii. ☐ will follow.

II. Other document(s) or information included:

11. ☒ An International Search Report (PCT/ISA/210) or Declaration under PCT Article 17(2)(a):

a. ☒ is transmitted herewith.

b. ☒ has been transmitted by the International Bureau.
Date of mailing (from form PCT/IB/308): 23.03.99

c. ☐ is not required, as the application was searched by the United States International Searching Authority. 23 March 1999

d. ☐ will be transmitted promptly upon request.

e. ☐ has been submitted by applicant on _____
Date

12. ☐ An Information Disclosure Statement under 37 C.F.R. §§ 1.97 and 1.98:

a. ☐ is transmitted herewith.

Also transmitted herewith is/are:

☐ Form PTO-1449 (PTO/SB/08A and 08B).

☐ Copies of citations listed.

b. ☒ will be transmitted within THREE MONTHS of the date of submission of requirements under 35 U.S.C. § 371(c).

c. ☐ was previously submitted by applicant on _____
Date

13. ☐ An assignment document is transmitted herewith for recording.

A separate ☒ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

Assigned to: Yissum Research Development Company of
The Hebrew University of Jerusalem

P.O. Box 4279, Jerusalem 91042 ISRAEL

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☒ 37 C.F.R. § 1.492(b), (c) and (d) (presentation of extra claims)

NOTE: Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.492(d)), it might be best not to authorize the PTO to charge additional claim fees, except possible when dealing with amendments after final action.

- ☐ 37 C.F.R. § 1.17 (application processing fees)
- ☐ 37 C.F.R. § 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a).
- ☐ 37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

NOTE: Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

NOTE: 37 C.F.R. § 1.28(b) requires "Notification of any change in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying . . . issue fee." From the wording of 37 C.F.R. § 1.28(b): (a) notification of change of status must be made even if the fee is paid as "other than a small entity" and (b) no notification is required if the change is to another small entity.

- ☐ 37 C.F.R. § 1.492(e) and (f) (surcharge fees for filing the declaration and/or filing an English translation of an International Application later than 30 months after the priority date).

Sandra M. Koenig

SIGNATURE OF PRACTITIONER

KOENIG, Sandra M.

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Tel. No.: (216) 861.5582

(type or print name of practitioner)

FAY, SHARPE, FAGAN, MINNICH & MCKEE, LLP

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF : Nissim Garti
FOR : **METHODS FOR THE PREPARATION OF
NANOSIZED MATERIAL PARTICLES**
SERIAL NO. : Unknown
FILED : Herewith
ATTORNEY DOCKET NO. : HES 2 0001

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, D.C. 20231
BOX PCT
Attention: EO/US

Dear Sir:

Prior to examination of the subject application, please amend the application
as follows:

In The Claims:

Please cancel **claims 1 - 11.**

Please add the following new **claims 12 - 30.**

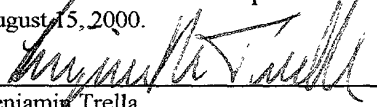
12. A method for the production of nanomaterial particles comprising the
steps of:

synthesizing nanomaterial particles in solutions of complex liquids from
suitable precursors, which precursors are selected from suitable surfactants and alkoxides, by
a suitable chemical reaction under mild conditions; and

preparing fine colloids dispersed in various polymer solutions.

Certificate of Express Mailing

I hereby certify that this Preliminary Amendment is being deposited with the United States Postal Service as Express
Mail Procedure in an envelope addressed to the Assistant Commissioner For Patents, Washington, D.C. 20231 on
August 15, 2000.


Benjamin Trella

Date: August 15, 2000

13. A method according to claim 12, wherein the water in the solution is nonfreezing water.
14. A method according to claim 12, wherein the nanomaterial particles have a diameter of 1-5 nm.
15. A method according to claim 12, wherein the mild conditions are atmospheric pressure and a temperature range of room temperature to 70°C.
16. A method according to claim 12, wherein the chemical reaction is a hydrolysis process.
17. A method according to claim 12, wherein the chemical reaction is a reduction process.
18. A method according to claim 12, wherein the chemical reaction is an exchange process.
19. A method according to claim 12, wherein the solution comprises an organized water-organic surfactant.
20. A method according to claim 12, wherein the solution comprises a microemulsion.
21. A method according to claim 12, wherein the solution comprises liquid crystalline media.
22. A method according to claim 12, wherein the solvent is selected from the group consisting of a suitable hydrocarbon, a chlorinated hydrocarbon and ether.

23. A method according to claim 22, wherein the hydrocarbons are selected from the group consisting of octane, decane and dodecane.

24. A method according to claim 22, wherein the chlorinated hydrocarbon is 1, 2-dichlorethane.

25. A method according to claim 22, wherein the ether is ethylether.

26. A method according to claim 12, wherein the surfactants are selected from the group consisting of trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB); sodium bis-(2-ethyl-hexyl)-sulfosuccinate; and poly-ethoxyethylene-10-oleyl ether.

27. A method according to claim 12 wherein metal oxides and metal precursors are selected from the group consisting of triethoxy silanes (TEOS); trimethoxy silane (TMOS); Al, Zr isopropoxides; Fe, Mg and Al chlorides; Al and Mg acetates; Na and K orthosilicates; Zr oxychloride and transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt.

28. A method according to claim 12, wherein the polymers are selected from the group consisting of polyethylene oxide (PEO); polyvinyl chloride (PVC); polyvinyl alcohol (PVA); and polymethyl methacrylate (PMMA).

29. A method according to claim 17, wherein the reducing agent is selected from the group consisting of sodium formate; hydrogen; and alcohol.

30. A method according to claim 29 wherein the alcohol is selected from the group consisting of methanol, ethanol, and isopropylalcohol.

REMARKS

Prompt and favorable examination of the subject application is earnestly solicited.

Respectfully submitted,

FAY, SHARPE, FAGAN,
MINNICH & MCKEE, LLP

Date: Aug. 15, 2000

Sandra M. Koenig
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2000 AUG 15 10 00 AM

METHODS FOR THE PREPARATION OF NANOSIZED MATERIAL PARTICLES

The present invention relates to the methods for the preparation of nanosized material particles. ("Nano-materials" in connection with the present invention comprise transition metals and alloys; metal oxides; and ceramic compositions having a small nanosize, i.e. about 1 - 6 nm.) Nanomaterials are prepared from the corresponding precursors i.e. the corresponding metal salts or alkoxides by suitable chemical reactions, e.g. reduction, hydrolysis and exchange processes under mild conditions.

There are known methods to prepare clusters or fine colloids from said nanomaterials which are dispersed in different suitable solutions. Appropriate liquid media enable the production of different preparations, which may be used as thin films on various supports.

There are known several methods for the preparation of ultrathin films of metal particles on solid supports, e.g. ion implantation (M.Che. C.O. Bennet, Adv. Catal. 1989, 36, 55); organometallic chemical vapor deposition (A. Sherman, Chemical Vapor Deposition for Microelectronics, Principles, Technology and Application, Noyes Publications; Park Ridge, N.J. 1987; and N.H. Dryden et. al., Chem. Mater. 1991, 3, 677); metal deposition from colloidal solution (G.Schmid, Chem. Rev. 1992, 92, 1709); reductive metal deposition from aqueous salt solution (I.Coulthard, et. al., Langmuir 1993, 9, 3441.); photodecomposition of metal complexes in thin films (R.Krasnasky et. al. Langmuir, 1991, 7, 2881); and photo-reductive deposition from Pd(II) complexes in solution (K. Kondo et. al., Chem. Lett. 1992, 999) Other technics are based on the film formation of noble metal loaded block copolymers (Y.NgCheongChan et. al., Chem.Mater. 1992, 4, 24; and J.P.Spatz, et al., Adv. Mater. 1995, 7, 731.); on the Langmuir-Blodget (LB) transfer of monolayers or surfactant stabilized metal colloids (F.S. Meldrum et. al., Langmuir 1994, 10, 2035; and F.S. Meldrum et al., Chem. Mater. 1995, 7, 1112); and on thermal decomposition of LB films of zero valent palladium complexes (E.

Maassen et. al., Langmuir 1996, 12, 5601).

At present the microelectronic and some related industries, mainly continue to use the vapor deposition method. The "Wet" method, which is a method of film deposition from solutions, provides a good challenge for the industry since it does not require high temperatures and pressures or high vacuum and enables to vary the properties of the nano compositions to a large extent

During the last decade, the number of scientific works devoted to the synthesis of nanomaterials in solutions has significantly increased. Certain practical results were reported. Thus, for example G. Schmid (see above) demonstrated that the pellets which consist of ligand stabilized golden clusters (derived from a liquid) may be regarded as tunneling resonance resistors and, additionally, as cellular automates. The density of electronic switches, compared with common semiconductors increased in another example to a factor of 10^5 - 10^6 . Another paper (T. Yamamoto, in Macromolecular Complexes, Ed. by Eishun Tsuchida, VCH, 1993, 380-395.) informed about the preparation of electrically conducting polymer compositions by using organosols of metal sulfides. The polymer-composite films not only show good electrical conductivity but were also controlled to p- or n-type conductors.

The realization of quantum dots, of uniform size and structure opens the door to multiple switches. This enables the manufacture of new generations of computers with extremely high capacities. The manufacture of novel mini-lasers, based on quantizing particles, will most probably lead to optoelectronic switches, operated simultaneously by photons and electrons. Nanometal coatings may be effectively used, e.g. as film catalysts (for instance in the processes of electroless metal deposition); and as modifiers of mechanical properties of different materials.

However, all said conventional methods are not satisfactory in the preparation of coatings comprising nanomaterial particles, as they are rather complicated, expensive or do not yield the particles having the desired size.

It has thus been desirable to find a method which would

overcome said disadvantages, i.e should not be complicated, not be too expensive and yield nanomaterial particles having the desired size.

It is well known that water which appears to be a key factor which governs the association of surfactants in different solvents, functions not only as an inert solvent but plays a significant part in the mechanism of chemical processes. (Garti et. al. Coll. & Interface Sci. 178 (1996) p. 60-68). When describing the state of water in relation to any surface a distinction is usually made between "bulk" and "bound" water. It is assumed that "bulk" or free water has physico-chemical properties which are not very different from those of pure water. "Bound" water may be defined by the operational definitions which refer to the water detected by a certain technique.

According to the method utilized by Senatra (D. Senatra et. al. Can. J. of Phys. 68 (1990) p. 1041), in which the endothermic scaling mode was applied and the peaks representing various states of water were identified and analyzed, it was shown that "free" water melts at 0°C, "interfacial bound" water melts at -10°C, and non-freezing water which is the most strongly bound part of bound water has no peaks on thermograms up to -100°C.

It has been found that the state of the water in water-organic-surfactant organized solutions is strictly correlated with the size of the particles. Particles which have a diameter of less than 5 nm are synthesized in systems which comprise only strongly bound water (non freezing water according to subzero differential scanning Calorimetry DSC).

In developing the method according to the present invention it has been considered:

a. producing the water-organic-surfactant organized solutions (complex liquids) comprising nanosized particles in particular having a diameter of 1- 5 nm which are useful for the particle preparation;

b. regulating the water content in such a manner that the whole water will be strongly bound to the surfactant (non-freezing) in the system, thus enabling to provide nano particles which have a diameter of less than 5 nm;

c. the regulation of the solution structures which enables

the regulation of the morphology of the particles;

d. the variation of the chemical composition and concentration of nano-precursors (and of the complementary reactants), which enables the control of the particle size distributions (PSD) and of the thickness of the protecting shells;

e. using different polymers which enable the production of films having different adhesion properties, by the deep coating method; and

f. the control of the viscosity and of the velocity of the solutions which lead to different film thicknesses;

The optimization of the above-mentioned factors (which should operate simultaneously) should lead to the production of the coating having the desired properties.

The present invention thus consists in a method for the production of nanomaterial particles (as herein defined) in which:

said nanomaterial particles are synthesized in the solutions of complex liquids containing non-freezing water from suitable precursors, which precursors are selected from suitable surfactants, metal salts and alkoxides by a suitable chemical reaction under mild conditions; and

preparing from said materials fine colloids dispersed in various polymer solutions.

The nanomaterial particles have advantageously a diameter of 1-5 nm.

The water in the solution is advantageously non-freezing water as determined by low temperature differential scanning calorimetry

The suitable chemical reaction may be selected, for example, among reduction, hydrolysis and exchange processes.

Mild conditions in connection with the present invention are suitably atmospheric pressure and a temperature range of room temperature to 70°C.

Suitable solutions may be selected among suitable water-organic-surfactant solutions; (microemulsions; liquid crystalline media; etc.)

Suitable organic solvents may be, e.g. selected among

suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloroethane); ethers (ethylether); etc.

The appropriate liquid media enable the preparation of different self assemblies of nanomaterials and subsequently the use of them as thin films on various supports.

Suitable surfactants are, for example,:

Quaternary ammonium salts, e.g. trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB), etc.; sodium bis-(2-ethyl-hexyl)- sulfosuccinate; poly-ethoxyethylene-10-oleyl ether (Btj 96; etc.

Oxide precursors may be, e.g.

alkoxides:

tetraethoxy silane (TEOS); tetramethoxy silane (TMOS); Al, Zr isopropoxides, etc;

Fe, Mg and Al chlorides; Al and Mg acetates; Na and K orthosilicates; Zr oxychloride; etc. Metal precursors may be, e.g. transition metal salts of Fe, Co, Ni, Cu, Ru, Rh, Pd, Ir and Pt, e.g. FeCl_3 , K_2PdCl_4 , K_2PtCl_4 and CuCl_2 .

The polymers may be selected, e.g. from polyethylene oxide (PEO), polyvinyl chloride (PVC), polyvinyl alcohol (PVA), polymethyl methacrylate (PMMA), etc.

Suitable reducing agents are, for example, sodium formate; hydrogen; certain alcohols (methanol, ethanol, isopropylalcohol); etc.

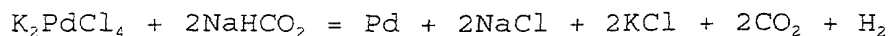
The method according to the present invention can direct the morphology, dimension and homogeneity of the size distributions of the small colloids (and clusters) and also their self assembling.

Example 1

A Pd colloidal dispersion was prepared from a solution containing 12% wt of hydrated trioctylmethylammonium chloride (aliquat 336) which corresponds to water/aliquat molar ratio = 3.06. Sub-zero DSC analysis did not reveal any peak which belongs to interfacial (-10°C) and free water (0°C) in the precursor solution.

Potassium tetrachloropalladate (K_2PdCl_4) (326mg) was solubilized in a 5 ml aliquat-dichloroethane-water mixture. Sodium

formate (NaHCO_2) (0.22 gr) was poured onto the mixture under argon. The reaction was carried out in accordance with the following formula:



The reaction was carried out at 75°C . In the course of the reaction, the orange color gradually changed to a dark brown color. The reaction was stopped after 1 hour and the dichloroethane was evaporated from the reaction mixture. The waxy residue obtained, was washed, in order to remove the inorganic salts, with deionized water and dried at 30 torr and 60°C .

Electron diffraction data revealed a face centered-cubic (fcc) Pd phase, while Transmission Electron Microscopy (TEM) analysis showed round particles having a mean diameter of 1.8 nm.

The nanometal prepared was redispersed in 40 ml of dichloroethane containing 30% of a v/v Polyvinyl alcohol (PVA). The viscosity of the solution was 40 cps.

The surface of a glass plate was thoroughly cleaned with hot water, methyl alcohol and diethyl ether. A coating was prepared by drawing with the velocity of 8 mm/sec. The bright orange transparent film obtained had a magnitude of electrical conductivity $10^{-8} \Omega^{-1}\text{cm}^{-1}$.

Example 2

1.25 g of a commercially available nonionic surfactant Brij-96 (poly-ethoxyethylene-10-oleyl ether $\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)\text{OH}$ (PEO) was added to a mixture of 4 ml of hexane and 1.18 g of i-butanol. 1 ml of a 0.025M solution of FeCl_2 in 0.01 HCl was then poured on the mixture. The mixture was homogenized by Vortex and it then looked like a homogenous solution. The sub-zero DSC analysis did not reveal any peak which belong to freezing water. After an ageing process at 40°C in the course of 48 hr, TEM and small angle X-ray scattering (SAXS) there were visualized particles having a mean diameter of 3.5 nm and 10% degree of polydispersion. Photoelectronic Spectroscopy (XPS) analysis indicated FeOOH formation. The microemulsion was concentrated by evaporation at 35°C and 60 torr and the wax residue obtained was redispersed in 10 ml of Polyethylene glycol (PEO). The viscosity of the solution was 9.3 cps. A coating was prepared by drawing with the velocity

of 12 mm/sec. Corning glass plates were soaked in ethanol solutions in the course of 24 hr rinsed with distilled water under sonication, then immersed in ethanol and dried at 105°C for 8 hr. A film was formed on the glass plate by spreading of the solution. After a film heat treatment at 45°C the film was not cracked or destroyed. Scanning electron microscopy (SEM) of the coating (removed from the support) did not show any growth of the particles.

Example 3

0.5 g of commercially available surfactant didodecylammonium bromide (DDAB) containing 6% of water was added to 7 ml of toluene, and stirred with shaking to form an inverse micellar solution. Thereafter 0.025 g of K_2PtCl_6 and 1.2 ml of tetraethylo-rthosilicate (TEOS) were added to the solution obtained, which was then stirred until the salt was fully solubilized. Then $NaBH_4$ was poured into the salt precursor solution with rapid stirring in an argon atmosphere so that the $[BH_4]:[Pt^{4+}]$ relation was 4:1. The solution gradually turned to dark brown. The pH of the solution was adjusted to 6.5 by the addition of an organic buffer in ethanol. The solution was aged at room temperature during 3 days previous to film formation by deep coating. According to sub-zero DSC data, the system did not contain any freezing water. The viscosity of the solution was 7.2 cps. A coating was prepared by drawing with the velocity of 12 mm/sec.

Glass substrates were cleaned in the same manner as described in Examples 1 and 2. In order to enhance the adhesion of the film to the glass, cleaned and dried glass supports were immersed in a 0.5% ethanol solution of triaminopropyltriethoxysilane, rinsed with dichloromethane and ethanol and baked in an oven at 120°C for 2 hr. SAXS, TEM, XPS and SEM analyses were indicative of nanosize (3-5 nm) Pt (partially oxidized on the surface) particles embedded in the silica matrix. Low temperature nitrogen adsorption of the separated film dried at 100°C in the course of 3 hr showed 37% film porosity having a mean pore diameter of 35Å°. Thermo treatment of the film at 450°C for 1 hr did not change the pore characteristics of the film. Such prepared substrates were suitable in electroless Ni plating. A

[illegible]

Claims.

1. A method for the production of nanomaterial particles (as herein defined) in which:
said nanomaterial particles are synthesized in the solutions of complex liquids from suitable precursors, which precursors are selected from suitable surfactants, metal salts, and alkoxides, by a suitable chemical reaction under mild conditions;
and preparing from said materials fine colloids dispersed in various polymer solutions.
2. A method according to Claim 1 wherein the water in the solution is non freezing water.
3. A method according to Claim 1 or 2, wherein the nanomaterial particles have a diameter of 1-5 nm.
4. A method according to any of Claims 1 to 3, wherein the mild conditons are atmospheric pressure and a temperature range of room temperature to 70°C.
5. A method according to any of Claims 1 to 4, wherein the chemical reaction is selected among a hydrolysis, reduction and exchange process.
6. A method according to any of Claims 1 to 5, wherein the solutions are selected among organized water-organic-surfactants (microemulsions and liquid crystalline media).
7. A method according to any of Claims 1 to 6, wherein the solvent is selected among suitable hydrocarbons (octane, decane, dodecane); chlorinated hydrocarbons (1,2 - dichloroethane); and ethers (ethylether).
8. A method according to any of Claims 1 to 7, wherein the surfactants are selected among trioctylmethyl ammonium chloride (aliquat 336), dioctyldimethylammonium bromide (DDAB), cetyltrimethylammonium chloride (CTAB); sodium bis-(2-ethyl-hexyl)- sulfosuccinate; and poly-ethoxyethylene-10-oleyl ether.
9. A method according to any of Claims 1 to 6, wherein metal oxides and precursors are selected among tetraethoxy silanes (TEOS); tetramethoxy silane (TMOS); Al, Zr isopropoxides,;
Fe, Mg and Al chlorides; Al and Mg acetates; Na and K

10. A method according to any of Claims 1 to 9, wherein the polymers are selected among polyethylene oxide (PEO); polyvinyl chloride (PVC); polyvinyl alcohol (PVA); and polymethyl methacrylate (PMMA).
11. A method according to any of Claims 5 to 10, wherein the reducing agent is selected among sodium formate; hydrogen; and certain alcohols (methanol, ethanol, isopropylalcohol).

A B S T R A C T

The present invention relates to a method for the production of particles of nano-materials being transition metals and alloys; metal oxides; and ceramic compositions having a small nanosize, i.e. about 1 - 6 nm. The method comprises a synthesis in the solutions of complex liquids from suitable precursors, which precursors are selected from suitable surfactants and alkoxides, by a suitable chemical reaction under mild conditions; and preparing from said materials fine colloids dispersed in various polymer solutions. The water in the solution is preferably non freezing water, the mild conditions are atmospheric pressure and a temperature range of room temperature to 70°C, and the reaction condition is selected among a hydrolysis, reduction and exchange process.

DECLARATION FOR PATENT APPLICATION

As the below named inventors, we hereby declare that:

Our residences, post office addresses, and citizenships are as stated below next to our names.

We believe we are the original, joint, and first inventors of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHODS FOR THE PREPARATION OF
NANOSIZED MATERIAL PARTICLES

the specification of which is attached hereto.

We hereby state that we have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

We hereby claim foreign priority benefits under Title 35, United States Code § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

International (PCT) Application No. PCT/IL99/00057,
Filed February 16, 1999

Israel Patent Application No. 121462,
Filed February 26, 1998

We hereby claim benefit under Title 35, United States Code § 119(e) of any United States provisional applications listed below:

None

We hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112. We acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

None

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